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METHOD AND DEVICE FOR SURFACE-TREATMENT OF SUBSTRATES

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The invention concerns a method and device for surface treatment of substrates with the aid of a gas discharge.

In surface treatment of flat substrates by means of a gas discharge, such as low-pressure glow discharges, methods are known in which the discharge is maintained by means of a microwave antenna, a high-frequency electrode, or a pulsed or timewise continuous voltage, applied to the substrate. Substrate surfaces and counter-electrodes and microwave antennas are thereby mostly arranged opposite each other.

A critical disadvantage of this method is that as a rule, only a low plasma density can be generated and the rate of plasma cleaning or plasma coating of the substrate surface is therefore low. Although the plasma density can be also be increased by increasing the pressure, the associated decrease in the mean free path leads to the transport of materials to and from the substrate surface being strongly hindered. In addition, the tendency of the discharge to local contraction and instability grows. Also disadvantageous in this method is the fact that an undesirable coating of microwave-coupling windows or high-frequency electrodes arises, whereby the coupled power clearly decreases over time.

Also disadvantageous is the fact that large amounts of starting materials are thereby lost and that other internal surfaces of the vacuum chamber become coated in addition to the substrate.

Surface treatment of running metal bands, such as sheet steel or aluminum, activated or supported by an electric gas discharge, presents special problems in batch processes involving the treatment of substrates.

On the one hand, the high running speed of the band requires very high stationary coating rates and plasma densities, for sheet steel up to a rate of 100 m/min. For example, in order to deposit a coating thickness of 100 nm at a band speed of 100 m/min and a coating-zone length of 1 m, a stationary coating rate of 10 µm/min is required. This is about 2 orders of magnitude more than can be achieved with ordinary DC or AC glow discharges.

Plasma densities as high as possible are also to be strived for in order to achieve higher deposition rates for effective removal rates for surface contaminants (oils, fats, waxes) with formation of gaseous products on a rapidly running band. Ordinary glow discharges generally do not have a sufficient degree of ionization and have too low a proportion of active species such as oxygen atoms or hydroxyl radicals.

In addition to providing high plasma densities, production systems of this kind are expected to be able to be operated for several days without maintenance. A condition for this is that parasitic deposition of layers, i.e. the growth of layers in other places than on the sheet metal to be treated, be kept low. It should be considered that in 100 h the hypothetical "stationary" layer thickness on sheet metal at rest is up to 6 cm at a growth rate of 10 μm/min. Even if the parasitic growth rate on a counter-electrode, a deflector, or housing wall is only 1% of this value, the resulting layers with layer thickness of 600 μm would be unacceptable, since because of their internal tensions they would no longer adhere to their substrates and would disturb the coating process in the form of dislodged chips.

p7 Starting from these and other disadvantages of the state of the art, the invention is based on the task of providing a method and a device for surface-treatment of substrates, which, in addition to high plasma densities, also provides a concentration of the high plasma densities in the immediate neighborhood of the surface to be treated, with simultaneous reduction of parasitic deposits. In addition, the coating of both moving substrates, e.g. bands, and stationary substrates is possible.

~~This task is solved with respect to process technology by Claim 1, and, concerning a device to perform the process, by Claim 16. The subclaims in each case give advantageous embodiments and further refinements of the invention.~~

In order to restrict gas discharges spatially to the surfaces to be treated, one or more electrically conducting substrates or substrates that have been coated on at least two sides to make them conducting are used so that a concentrated plasma with high plasma density is formed in the immediate neighborhood of the substrate surfaces. Through local restriction of the discharge, parasitic effects on surfaces not to be treated are strongly reduced. The discharge preferably involves a glow discharge.

p8-7 ~~The restriction of the discharge region occurs preferably on at least two essentially~~ opposite sides, and can be, for example, in the form of a cylinder [~~sic, prism~~] with round or polygonal cross section, depending on the shape ~~of the substrate~~ to be coated. It is also especially appropriate to enclose it between ~~two flat~~ substrates arranged parallel to one another. Regardless of the shape of ~~the enclosure~~, the distance between the opposite surfaces in each case should be ~~about 1 mm to 50 cm, preferably 1 cm to 10 cm.~~

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In addition to surface treatment of stationary substrates in a batch process, the process according to the invention is especially suitable for treating continuously moving substrates, for example, materials in the shape of a band. Here, the discharge region is restricted by having one or more substrate bands pass, at least in some regions, with a short distance from the gas discharge and thereby restrict the discharge region. Thus, for example, two bands can be fed

parallel to each other in some regions and the stationary gas discharge is enclosed by one of the band surfaces to be treated each time.

sub F2

Especially advantageous is the surface treatment of one or more band-shaped substrates, which are turned while changing their direction of movement at least once and restrict the discharge region, at least on the one hand, by means of a surface region that lies before the turn in the direction of the band movement, and on the other hand, by means of a surface region that lies after the turn in the direction of the band movement. In this way, the surfaces of the band-shaped substrate to be treated pass the discharge zone at least twice each time the band is fed. A surface treatment made much more intense in this way permits an advantageous increase in the rate of movement.

The electric discharge preferably involves a discharge in the region of the hollow-cathode discharge. By this, according to the invention, is also understood a discharge in the transition region between hollow-cathode discharge and normal discharge. The entire substrate, which can be at ground potential, thereby forms the cathode. An anode, which is at a positive potential with respect to ground, is located as a counter-electrode in an appropriately selected site in the apparatus, preferably at the edge of the gas discharge. Even with a microwave-activated discharge, a hollow-cathode discharge can be constructed. The plasma then forms a "virtual" anode.

A hollow-cathode discharge is significantly more intense than an ordinary glow discharge between a cathode and an anode arranged parallel to each other. Ionization an order of magnitude higher is achieved, and significantly higher corresponding coating and removal rates are achieved. The hollow-cathode discharge is formed by use of a DC or AC voltage when the substrate surfaces restrict the discharge region to the shape of a hollow space, i.e. on at least two sides, and suitable process parameters (pressure, distance of the substrate surface, voltage, etc.) are chosen depending on the substrate geometry or the geometry of the discharge region. A hollow-cathode discharge between, e.g., two parallel plates appears as a clearly higher discharge current in comparison to the sum of the currents at each separate discharge at each of the two plates.

An electric discharge can be also realized, in addition to a DC or AC voltage, by coupling microwaves in the discharge region. For this, the discharge region defined by the substrate surface has a geometry that favors the spread of the microwaves in certain spatial regions and the formation of a gas discharge by achieving a stronger electric field. Preferably, the discharge region also has a hollow spatial geometry; in which case, the dimensions of the hollow space are adapted to the wavelengths of the microwave radiation used. As a further refinement, one can envision feeding microwaves and an electric voltage, preferably a DC voltage, into the discharge region simultaneously.

Supply and removal of gas take place directly in the discharge region or at a negligible distance from it. By a suitable arrangement of the gas supply and removal, the discharge can be restricted to the immediate planned discharge region between the substrate surface, and parasitic discharges are strongly reduced. Preferably, the means of gas supply and removal are arranged on the side opposite the discharge region, so that a permanent flow can be maintained.

Additional advantages and further refinements of the invention can be seen in the figures and the embodiment examples described below. Shown are:

Figure 1 shows implementation of a process according to the invention using a continuously running band-shaped substrate;

Figure 2 shows implementation of a process according to the invention using two continuously running band-shaped substrates;

Figure 3 shows implementation of process according to the invention using two stationary substrates; and

Figure 4 shows implementation of the process according to the invention using a continuously running substrate that is surrounded by a deflecting element.

The substrate 1 shown in Figures 1, 2, and 4 involves aluminum sheet metal 0.15 mm thick and 50 cm wide, in the shape of a band and supplied continuously. Other substrates, for example, steel or materials that have been coated so as to be conducting, can also be treated likewise. The substrate 1 in Figure 3 involves two stationary, parallel plates.

If the treated substrate 1 is heated too strongly, it can be cooled during surface treatment. The cooling can take place by means of a cool body through which a liquid or gaseous cooling medium flows and is in direct physical contact with the substrate. With stationary substrates, cooling can occur by means of cooling plates; and with moving substrates, by means of cooling rollers.

~~Substrate 1 can be grounded or connected to the ungrounded output of a voltage source. The voltage between substrate and a plasma formed by the electric discharge is preferably between 1 and 3000 V, more preferably, between 100 and 1000 V. Pulsed DC voltages with a pulse frequency between 10 kHz and 100 kHz can also be considered as DC voltages. When low-frequency AC voltages are used, the frequency is preferably between 50 and 60 Hz, and with intermediate-frequency AC voltages preferably between 10 and 100 kHz. High-frequency AC voltages preferably have frequencies between 1 and 50 MHz. Instead of or in addition to supplying power with a voltage source, it can also be supplied by microwaves. The microwave frequencies are preferably in the GHz range.~~

All arrangements shown in Figures 1 through 4 are, together with possible spools for winding and unwinding the band(s), placed in vacuum chambers (not shown). When band-shaped substrates are used, the substrate can also be moved to and from the discharge

region 2 by spools and vacuum locks outside the vacuum chamber. The discharge runs preferably at a pressure between 0.01 mbar and 100 mbar, especially preferably between 0.1 and 5 mbar.

Through gas lines 3 (not shown in Figures 3 and 4), inert gases such as argon, reactive gases, or even gas mixtures are introduced into the vacuum chamber. Reactive gases that can be considered include, for example, oxidizing, reducing, or carbon-containing or silicon-containing gases, such as oxygen, hydrogen, nitrogen, methane, acetylene, silane, hexamethyldisiloxane, tetramethylsilane, etc. With the aid of the reactive gases, for example, layers can be applied and materials can be removed, or gaseous components can be integrated into the surface regions. Thus, substrate surfaces can be cleaned of impurities such as lubricants, corrosion-protection agents, or oxide layers, or can be provided with corrosion-protection layers, adhesive layers for subsequent coatings, anti-friction layers to improve shaping properties, or decorative layers.

Gas removal lines 4 (not shown in Figures 3 and 4) from the vacuum chamber assure that products that might be deposited or applied from the discharge zone are removed without an opportunity to become deposited or applied parasitically.

Another possibility for reducing parasitic effects consists of arranging deflection elements, of sheet metal, for example, in the vacuum chamber. These deflection elements are electrically isolated from the components of the device and from the substrate in those regions of the vacuum chamber (chamber walls, flanges, etc.), where parasitic discharges could form because of the existing potentials, or else they enclose the discharge region and the substrate. In Figure 4, a deflection element of this kind is shown in the form of a metal cage 8.

Finally, other deflection elements, electrically isolated from device components and substrates, permit the sides of the discharge region that do not adjoin the substrate surfaces region to be sealed. Cracks remaining between these deflection elements and the substrates can be closed with an insulating material (oxide ceramic, heat-resistant plastic). By this means, it can be assured that only a small number of charge carriers can escape from the hollow space of the discharge region.

The geometric dimensions of the device shown in Figures 1, 2, and 4 will be explained in the following. The diameter of the upper, thick, turning roller 5 (Figures 1 and 4) is 50 cm and the diameter of the four lower rollers 6, arranged in a rectangle, is 16 cm. The horizontal distance between the axes of the lower rollers 6 and the vertical distance between the axes of the lower rollers 6 is 19 cm and 30 cm, respectively. A volume of about 30 x 50 x 3 cm, which is especially favorable for forming a hollow-cathode glow discharge, arises between parts of the aluminum sheet metal.

Gas supply 3 occurs according to Figures 1 and 2 through a stainless-steel tube 1 cm in diameter provided with 50 holes, each 0.7 mm in diameter. This stainless-steel tube is arranged parallel to the axes of the small rollers 6. Gas removal 4 occurs through a stainless-steel tube,

also provided with holes, below the lower pair of rollers. The stainless-steel tube for gas removal 4 has 100 2mm-diameter holes. Gas is pumped out by means of a Roots pump, which has an effective suction capacity of 500 m^3/h.

In Figures 1, 2, and 4, the sheet metal 1 supplied is electrically isolated from the housing and grounded. The gas-supply tube serves as the counter-electrode (anode). Either a DC voltage source (10 to 1000 V) or an intermediate-frequency voltage source (35 kHz, 500-V peak voltage) can be used as the voltage source. In Figure 3, a hollow-cathode discharge is activated by feeding in microwaves 9.

Embodiment Example 1: Cleaning

The entering sheet metal 1 is moistened with a foam of paraffin oil (about 0.5 g/m^2). The band speed is 10 m/min and the pressure is 0.5 mbar. Synthetic air (an oxygen/nitrogen mixture in a 1:4 ratio) is used as the gas with a volume flow of 4.5 m^3/h. At a DC voltage of 450 V, an intense discharge is formed between the metal pieces. After passing through the discharge zone, the sheet metal has on the side 7 to be treated a surface energy of 55 dynes/cm (determined with test inks). This confirms that the oil has been completely removed.

Embodiment Example 2: Plasma polymerization

In this example, the band speed is 20 m/min and the pressure is likewise 0.5 mbar. A mixture of argon and HMDSO (hexamethyldisiloxane) is used as the gas in a 10:1 partial-pressure ratio, and a total volume flow of 70 mbar [sic, mL] x 1/s (4.2 sLm) is used. By applying an intermediate-frequency voltage (500 V), a hollow-cathode discharge is formed between the metal parts. A plasma-polymer layer with a thickness of 53 nm is deposited on the surface of the sheet metal 7. The dynamic rate (product of band speed and layer thickness) of this system is about 1060 m x nm/min. On sheet metal at rest, the deposition rate is thereby about 30 nm/s.

Embodiment Example 3: Silicatization

Instead of the argon in Example 2, synthetic air is used with a volume flow of 60 mbar x 1/s. The band speed is 30 m/min. A silicon oxide layer with a thickness of 30 nm is formed. The dynamic rate is 600 m x nm/min, the static rate is 17 nm/s. The composition of the layer (according to EPMA) is $SiO_{1.7}C_{0.2}$. The surface energy (test inks) is over 58 dyne/cm.

7 ~~Claims~~

~~1. Process~~ for surface treatment of at least one electrically ~~conducting substrate or a substrate that~~ has been coated so as to be conducting, by means of a gas placed in the region of